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Pesticides in U.S. Streams and Rivers: Occurrence and Trends during 1992–2011

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During the 20 years from 1992 to 2011, pesticides were found at concentrations that exceeded aquatic-life benchmarks in many rivers and streams that drain agricultural, urban, and mixed-land use watersheds. Overall, the proportions of assessed streams with one or more pesticides that exceeded an aquatic-life benchmark were very similar between the two decades for agricultural (69% during 1992–2001 compared to 61% during 2002–2011) and mixed-land-use streams (45% compared to 46%). Urban streams, in contrast, increased from 53% during 1992–2011 to 90% during 2002–2011, largely because of fipronil and dichlorvos. The potential for adverse effects on aquatic life is likely greater than these results indicate because potentially important pesticide compounds were not included in the assessment. Human-health benchmarks were much less frequently exceeded, and during 2002–2011, only one agricultural stream and no urban or mixed-land-use streams exceeded human-health benchmarks for any of the measured pesticides. Widespread trends in pesticide concentrations, some downward and some upward, occurred in response to shifts in use patterns primarily driven by regulatory changes and introductions of new pesticides.

Over half a billion pounds of herbicides, insecticides, and fungicides were used annually during 1992 to 2011 to increase crop production and reduce insect-borne disease. However, pesticides also may have unintended consequences on water quality. A principal goal of the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program is to assess the occurrence of pesticides in U.S. streams and rivers. Another goal is to determine trends in pesticide concentrations in those same waters. Previous national summaries of studies by USGS have described pesticide occurrence in streams and rivers during 1992–2001[1–3] and concentration trends during 1992–2010.[4–6] This article highlights findings for streams and rivers across the conterminous U.S. (Figure 1) for the decade of 2002–2011 and compares them to previously

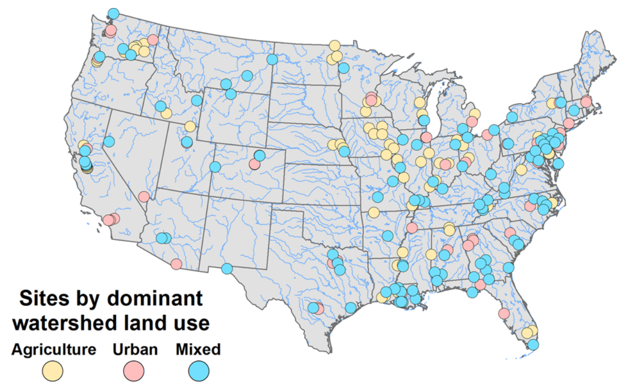

Figure 1. The national monitoring network for pesticides in streams and rivers included 182 sites during 1992–2001 and 125 sites during 2002–2011, with 96 of the sites common to both decades. Concentration trends were assessed for 39 major rivers with mixed land use and 27 urban streams.

reported findings from the decade of 1992–2001. Pesticide occurrence, potential significance to human health and stream ecosystems, and trends in stream concentrations of selected pesticides are summarized for the past 20 years—all focused on the most frequently detected pesticides among those measured. Supporting technical information for this summary is available in a series of USGS reports.[4–7]

PESTICIDES ASSESSED

During any given year, more than 400 different pesticides are used in agricultural and urban settings.[8] Not all pesticides in use or all streams and rivers can be measured because of budget constraints, limitations of analytical methods, and the constant changes in pesticide use, including the phasing out of some and the introduction of others. This study assesses a selected subset of pesticides in use over the last two decades that were sampled at enough sites to attain a reasonable national distribution and representation of land uses during 2002–2011.[7] The analysis includes 123 pesticide compounds analyzed in filtered water samples assessed during 2002–2011, of which 47 also were assessed during 1992–2001.[7] Figure 2 shows an overview by one measure, amount used, of how pesticides included in this decadal assessment relate to national total pesticide use and to selected pesticides or groups not included. A large portion of the difference between national total herbicide use and the proportion included in this assessment was the result of

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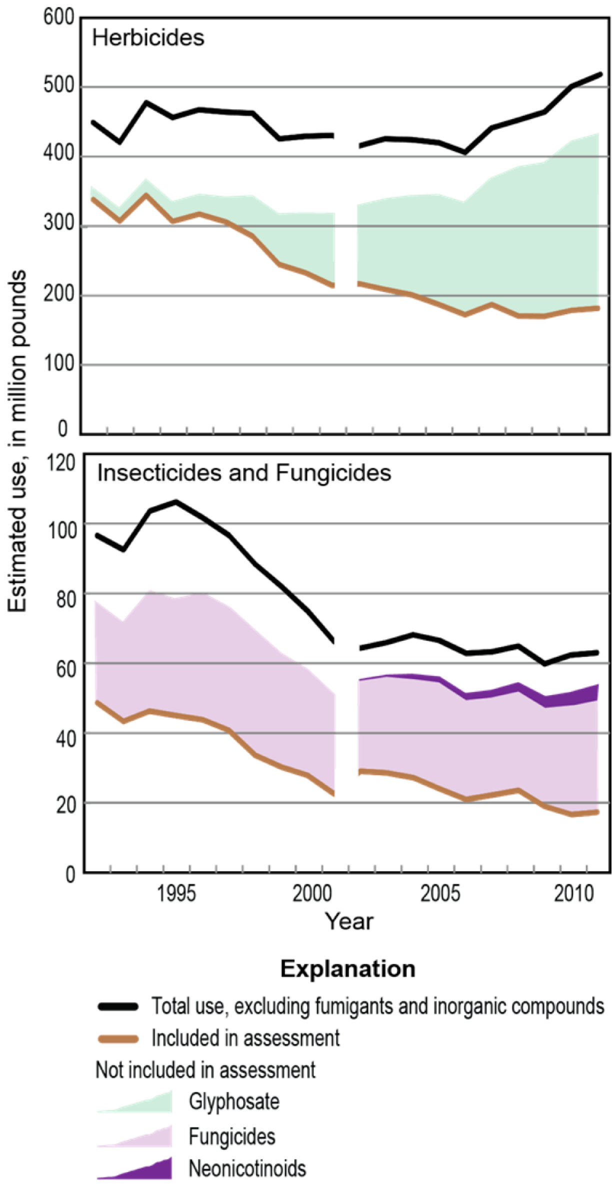

Figure 2. Nationally (conterminous U.S.), agricultural use of synthetic organic herbicides, insecticides, and fungicides had a peak in the mid-1990s, followed by a decline to a low in the mid-2000s.[7] During the late-2000s, overall pesticide use steadily increased, largely because of the rapid adoption of genetically modified crops and the increased use of glyphosate. The herbicides that were assessed by USGS represent a decreasing proportion of total use from 1992 to 2011 because glyphosate was not included in the national monitoring network (glyphosate has recently been added).

increased use of glyphosate that came with the rapid adoption of genetically modified crops resistant to glyphosate, beginning in the mid-1990s. Glyphosate is difficult and costly to measure and efforts to assess glyphosate have been limited primarily to regional, targeted, or short-term studies. Other types of pesticides not included in our assessment, such as neonicotinoid insecticides and most fungicides, are not individually as prominent as glyphosate in terms of amounts applied, but may be environmentally important because of their greater toxicity.

■ OCCURRENCE IN STREAMS AND RIVERS

For each of the past two decades, pesticides were found throughout most of the year (>95% of the time) in streams with agricultural, urban, and mixed-land-use watersheds.[7] The top 20 most frequently detected pesticides and their degradation products (composite of the top 10 from each land-use category and decade) show how the occurrences of individual pesticides in streams have changed between decades (Figure 3). These most frequently detected pesticides in the decadal comparisons include 11 herbicides (plus two degradates—deethylatrazine from atrazine and 3,4-dichloroaniline from triclocarban, diuron, linuron, and other herbicides), 4 insecticides (plus two degradates—desulfinylfipronil and fipronil sulfide, both from fipronil), and one fungicide—metalaxyl. Of these top 20 pesticide compounds: (a) five were not a part of the 1992−2001 assessment (registration and subsequent use occurred sometime during 1992−2001), (b) eight had similar detection frequencies between the two decades, with differences of 10% or less in terms of amount of time found in streams, and (c) seven pesticides (five herbicides and 2 insecticides), which are discussed below, had differences greater than 10% between the two decades in the amount of time detected in streams.[7] Note that four pesticides previously reported among the most frequently detected during 1992−2001,[1] bentazon, norflurazon, 2,4-D, and diuron, were not included in this decadal assessment because data for these pesticides had inadequate national distribution and representation of land uses during 2002−2011.

The herbicides alachlor, cyanazine, EPTC (*S*-ethyl dipropylthiocarbamate), Dacthal, and tebuthiuron were found in streams less frequently during 2002−2011 than during 1992−2001 (Figure 3), reflecting reductions in their use. Alachlor use steadily declined after the introduction and increased use of acetochlor in the mid-1990s. Cyanazine registration was voluntarily canceled in the mid-1990s and use rapidly declined after that. The agricultural use of EPTC, Dacthal, and tebuthiuron also declined.[6]

The organophosphate insecticides chlorpyrifos and diazinon also were found in streams less frequently during 2002−2011 than 1992−2001, especially in urban streams (Figure 3). Various uses of chlorpyrifos and diazinon began being phased out during the late-1990s and reductions in use, particularly in urban areas, continued into the early-2000s.[5] Simultaneously, fipronil registration and subsequent use in the U.S. began during the late-1990s, and it was used as an alternative to organophosphate insecticides for residential and commercial applications during the early-2000s. Fipronil was frequently detected, particularly in urban streams (63% of the time) during 2002−2011(Figure 3).

■ POTENTIAL CONCERNS FOR EFFECTS ON HUMANS OR AQUATIC LIFE

The potential for human-health concerns can only be approximated because this assessment represents untreated stream and river water from sites that are not located at drinking-water intakes. Annual mean concentrations were compared to human-health benchmarks for all pesticides assessed (not only the most frequently detected) to provide perspective on the potential significance to human health if the water were to be used as a source of drinking water.

During 1992−2001, 17% of agricultural streams and 5% of mixed-land-use streams had annual mean pesticide concentrations that exceeded human-health benchmarks.[7] During 2002−2011, only one agricultural stream and no urban or mixed-land-use streams exceeded human-health benchmarks for any of the measured pesticides. The pesticides exceeding

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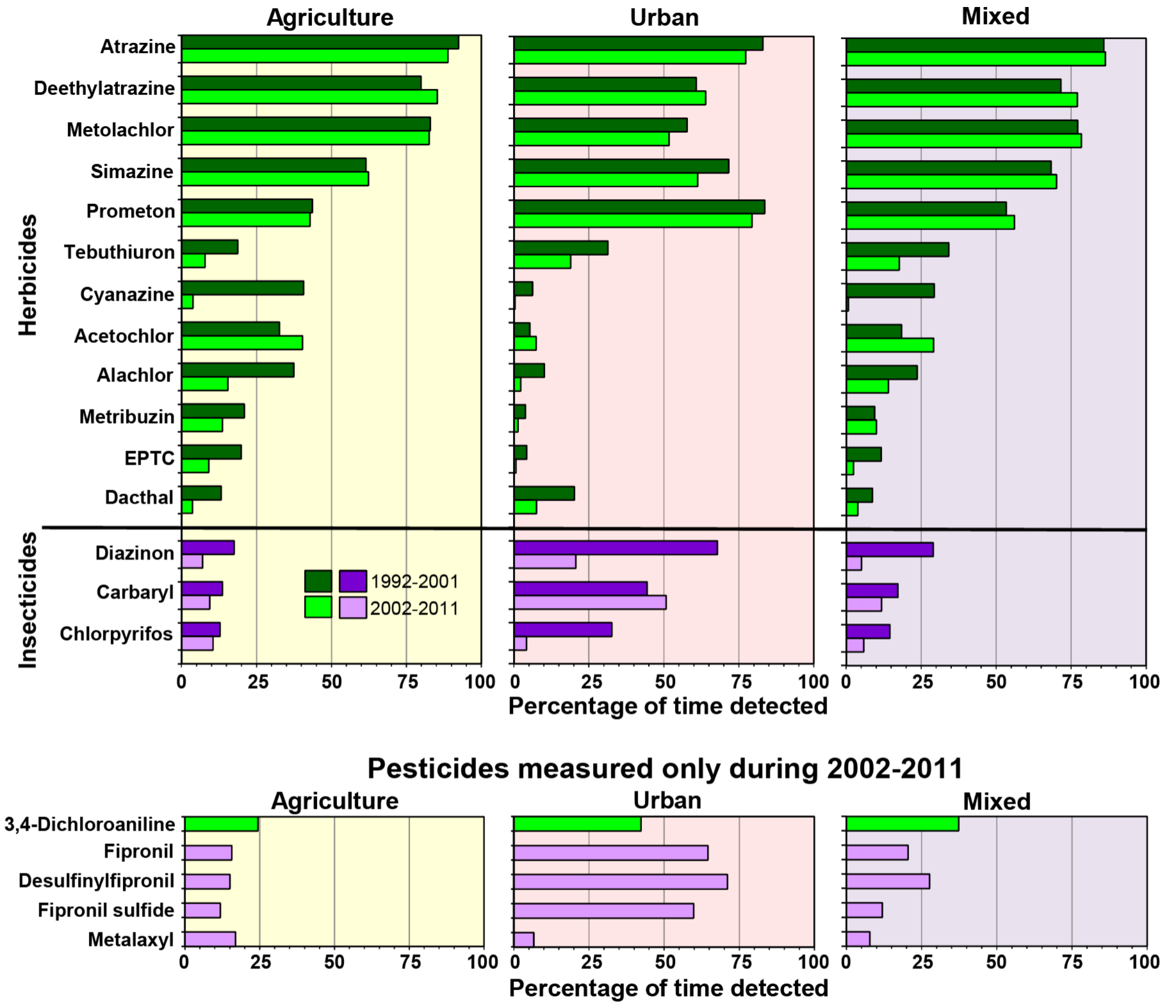

Figure 3. During 1992−2011, one or more pesticides were detected during most of the year in most streams draining agricultural, urban, and mixed land use watersheds. The most frequently detected pesticides varied between agricultural and urban land uses.

human-health benchmarks during 1992−2001 were α-HCH (lindane), atrazine, cyanazine, molinate, dieldrin, and propargite; whereas atrazine accounted for the only exceedance during 2002−2011. The decline in the number of streams and pesticides exceeding human-health benchmarks from 1992−2001 to 2002−2011 is consistent with regulatory changes and reductions in use between the two decades for these pesticides.[7]

Mean pesticide concentrations for appropriate durations were compared to chronic aquatic-life benchmarks for all pesticides assessed (not only the most frequently detected) to characterize potential for adverse effects on aquatic life. Potential concerns with acute exposure could not be assessed because the sampling frequencies were generally not adequate to reliably estimate acute exposures. Overall, the proportion of streams with one or more pesticides that exceeded an aquatic-life benchmark was similar between the two decades for agricultural and mixed-land-use streams, but much greater during 2002−2011 for urban streams (Figure 4). For all land-use settings, there were notable differences between decades in which pesticides most contributed to benchmark exceedances (Figure 5). The inclusion of the insecticides fipronil and dichlorvos during 2002−2011 accounted for most of the urban-stream exceedances, as exceedances by diazinon and other insecticides declined. Fipronil concentrations exceeded the chronic aquatic-life benchmark in more than 20% of agricultural and mixed-land-use streams and in 70% of urban streams during 2002−2011 (Figure 5). Weston and Lydy[9] recently confirmed the toxicity of fipronil and its degradates in urban streams.

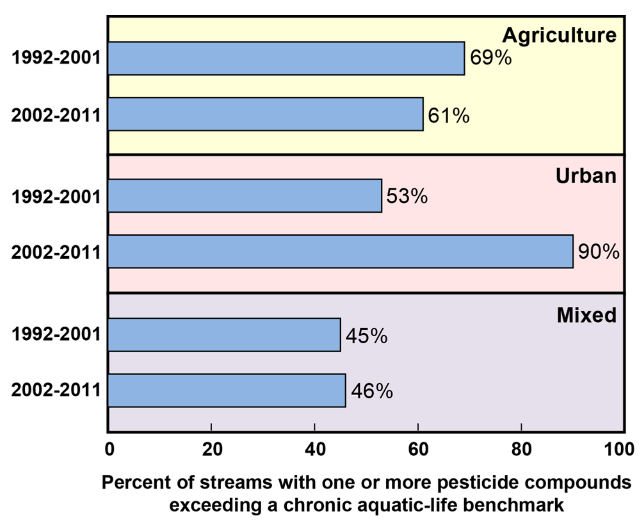

Figure 4. Proportion of streams with one or more pesticides that exceeded a chronic aquatic-life benchmark was very similar between 1992 and 2001 and 2002−2011 for agricultural and mixed-land-use streams, but much greater during 2002−2011 for urban streams.

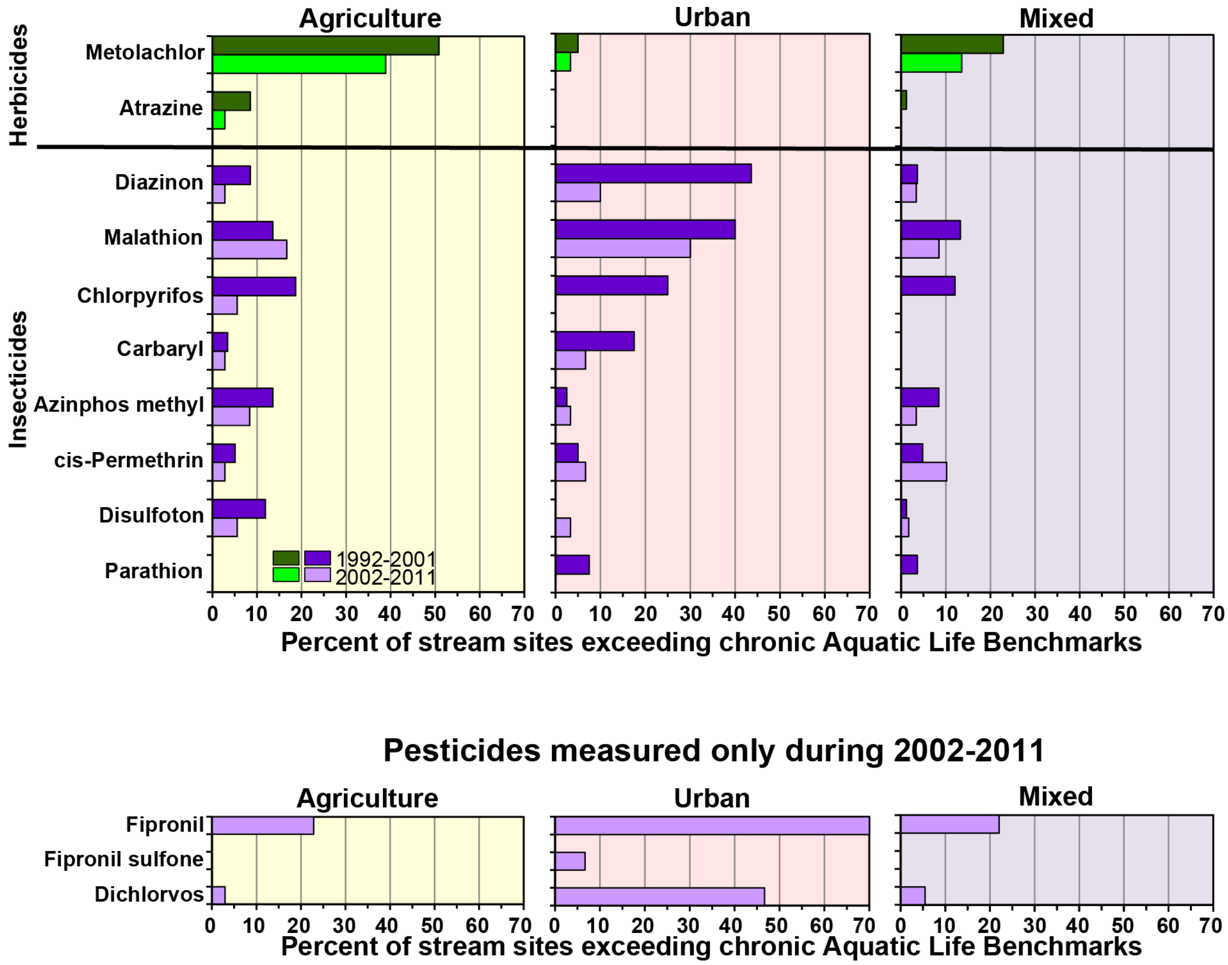

Figure 5. For pesticides that were assessed during both decades, the proportion of streams exceeding chronic aquatic-life benchmarks generally decreased from 1992−2001 to 2002−2011. This decrease was driven by reductions in use because of regulatory changes and market forces. Fipronil and dichlorvos, which were only measured during 2002−2011, accounted for the majority of exceedances in urban streams during that period.

Of the 10 pesticides with benchmark exceedances assessed in both decades (Figure 5), exceedance frequencies were mostly lower during 2002−2011. The herbicide metolachlor for all land-use settings, and the insecticides chlorpyrifos, diazinon, malathion, and carbaryl in urban streams, all had more than a 10% reduction from 1992−2001 to 2002−2011 in the proportion of streams exceeding a chronic aquatic-life benchmark.

TRENDS IN PESTICIDE CONCENTRATIONS OVER TIME

National concentration trends for seven pesticides that frequently exceeded chronic aquatic-life benchmarks and also have sufficient number of detections for trend analyses are summarized in Figure 6 for major rivers, mostly comparable to mixed-land-use streams in the occurrence assessment, and urban streams. The analysis of trends for 39 independent major rivers during 1997−2006 and 2001−2010 provides a national perspective on trends for large watersheds with mixed land uses.[6] Concentration trends in 27 urban streams across the U.S. were evaluated for 1996−2004 and 2000−2008.[5] The trend analyses evaluate seasonal patterns and multiyear trends at each site over the assessed time period, account for effects of varying hydrologic conditions at multiple time scales, estimate the magnitude and direction of trend, and statistically evaluate the significance of each trend. Trends were analyzed within partially overlapping 10-year periods because many of the changes in pesticide use happen within this time frame. The differing analysis periods between major rivers and urban streams reflects the availability of data when the analyses were done. Detailed results for site-by-site trends, significance, and magnitudes for these and other pesticides are provided in the cited publications.

Findings for the seven featured pesticides illustrate how various changes in occurrence, concentrations, and trends over a 20 year period combine to tell a unique story for each pesticide.

Metolachlor. Metolachlor, evaluated as the sum of metolachlor and *S*-metolachlor, is one of the most frequently detected pesticides and its concentrations frequently exceeded the *S*-metolachlor aquatic-life benchmark (the two forms of metolachlor have similar toxicities) during both decades in agricultural and mixed-land-use streams. Benchmark exceedances declined from 1992−2001 to 2002−2011, reflecting a sharp decline in use during 1998−2001 following the introduction of *S*-metolachlor, which requires about half the use rate for the same weed control. Consistent with its national use trend, concentration trends were predominantly downward or nonsignificant in major rivers during 1997−2006. Concentration trends then turned mostly upward during 2001−2010, corresponding to a gradual increase in use. Though use and concentrations increased during this recent decade, concentrations

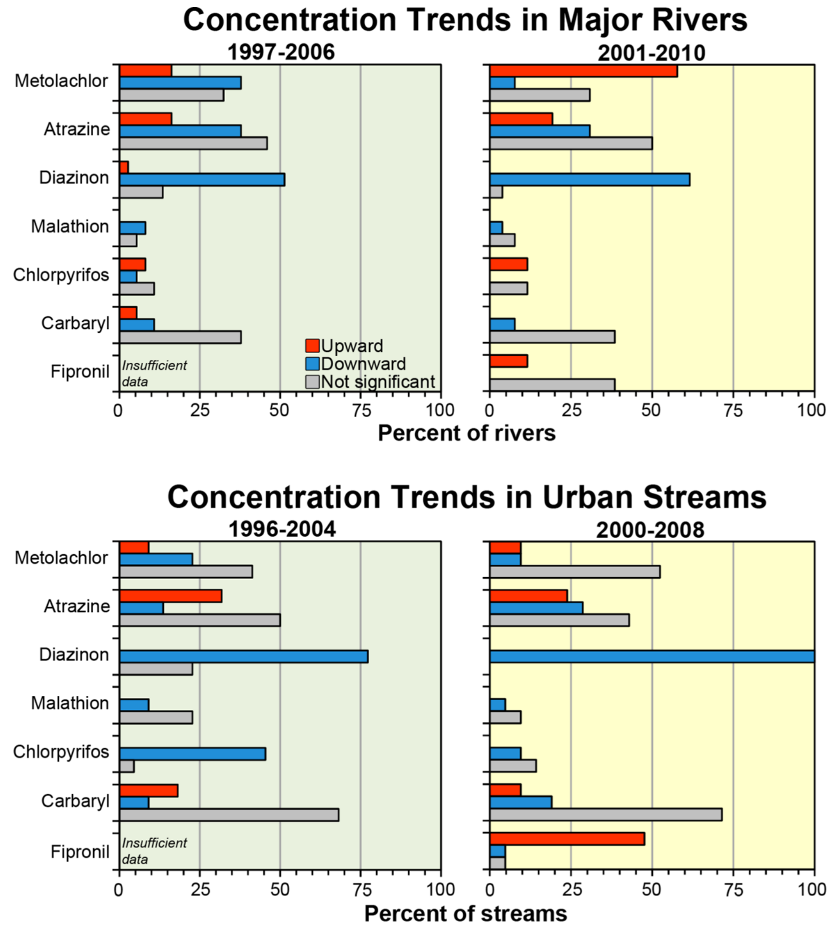

Figure 6. Statistically significant upward and downward concentration trends for seven pesticides that frequently exceeded chronic aquatic-life benchmarks generally followed use trends for 39 major rivers and 27 urban streams of the U.S. Sites with insufficient data were included to compute percentages, but are not shown.

remained lower than for most of the previous decade and were consistent with the lower frequency of benchmark exceedances during 2002–2011. Note that metolachlor had no available aquatic-life benchmark when earlier data were first analyzed[1−3] and, thus, provides an example of how assessments of potential significance and water-quality benchmarks can change with new information on potential effects.

Atrazine. Although atrazine has been one of the most frequently detected pesticides, its concentrations have been low compared to current aquatic-life benchmarks except in a small proportion of agricultural streams. In addition, benchmark exceedances declined from 1992–2001 to 2002–2011, consistent with the finding that concentration trends were predominantly downward or nonsignificant in major rivers during both 1997–2006 and 2001–2010. The national agricultural use of atrazine was relatively steady during 1997–2006 and gradually declined during most of 2001–2010.[8]

Diazinon. Diazinon has been most frequently detected in urban streams and exceeded its aquatic-life benchmark in about 45% of urban streams during 1992–2001. Exceedances declined to about 10% during 2002–2011. The decline in benchmark exceedances is consistent with the dominance of concentration downtrends in urban streams during both 1996–2004 and 2000–2008, and in major rivers during both 1997–2006 and 2001–2010. Agricultural use also declined during 1992–2010.[8]

Malathion. Malathion exceeded its aquatic-life benchmark in about 40% of urban streams and in more than 10% of agricultural and mixed-land-use streams during 1992–2001. Exceedances declined to about 30% in urban streams during 2002–2011. Although few sites could be tested for concentration trends during either assessment period because of the low frequency of detected concentrations, all testable trends were either downward or nonsignificant for both urban streams and major rivers. Agricultural use also declined during 1992–2010.[8]

Chlorpyrifos. Chlorpyrifos was frequently detected in urban streams and exceeded its aquatic-life benchmark in about 25% of urban streams during 1992–2001. Exceedances declined to none during 2002–2011. The decline in exceedances is consistent with the dominance of concentration downtrends in urban streams during both 1996–2004 and 2000–2008, although few trends were testable during 2000–2008 because of the increasingly low frequency of detection. Agricultural use also declined during 1992–2010,[8] but few major river sites could be tested for trends because of the infrequent occurrence.[6]

Carbaryl. Carbaryl was frequently detected in urban streams and exceeded its aquatic-life benchmark in almost 20% of urban streams during 1992–2001. Exceedances declined to less than 10% during 2002–2011. The reduced exceedances during 2002–2011 are consistent with the increased number of concentration downtrends and nonsignificant trends in urban streams during 2000–2008. Agricultural use also declined

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during 1992−2010,[8] and most concentration trends in major rivers were downward or nonsignificant during both decades.[6]

Fipronil. Fipronil exceeded its aquatic-life benchmark in 70% of urban streams, as well as in more than 20% of agricultural and mixed-land-use streams. Testable trends during 2002−2011 were mostly upward in urban streams and nonsignificant for major rivers. National agricultural use generally increased from 1998 to 2005 and then declined from 2005 to 2010.[8]

IMPLICATIONS AND NEXT STEPS

Pesticides assessed during 1992−2011, which represent somewhat less than half the amount of synthetic organic herbicides, insecticides, and fungicides used for agriculture in the U.S., frequently occurred in streams and rivers and pose continuing and widespread concerns for aquatic life based on benchmark exceedances. The potential for adverse effects is likely greater than these results indicate because a wide range of potentially important pesticide compounds were not included in the assessment. Recent regional studies in high-use areas, for example, indicate the likelihood that neonicotinoid insecticides[10] and fungicides[11] occur frequently in surface waters, but the environmental significance is not yet clear. In addition, sampling frequencies in this study were not adequate to reliably characterize the highest short-term concentrations and it focused on pesticides dissolved in water, whereas some hydrophobic pesticides, such as legacy organochlorines[2] and pyrethroid insecticides, are important as contaminants of sediment and tissues and should be considered when evaluating stream ecosystems. Pyrethroid insecticides have been found to be toxicologically important in both agricultural and urban affected streams.[12−15] Clearly, some of the pesticides not included in the present assessment may add substantially to overall occurrence and potential environmental significance. Expanded assessment should include additional pesticides that are currently used, improved characterization of short-term acute exposures, consideration of multiple environmental media (e.g., sediment and tissues), and coincident assessment of biological conditions. Results suggest that a relatively small proportion of individual pesticides in use may account for most of the concerns for aquatic life, based on comparisons to individual water-quality benchmarks. Thus, strategic design of laboratory analytical methods and sampling strategies needs to consider the toxicity, environmental fate properties, and use characteristics of all pesticides to ensure that the most critical pesticides and pesticide degradates are identified and tracked in future assessments.[16] Moreover, because complex mixtures of multiple pesticides are the most common mode of occurrence,[2] tracking co-occurrence and assessing the potential toxicity of mixtures[17] is vital to long-term success of future assessments.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

Notes

Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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